Simulation of Hydrate Agglomeration by the Discrete Element Method

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- Properties of Fuels, including Natural Gas Systems

Abstract

The accurate prediction of hydrate plug location and time of occurrence is an important piece of information for the successful operation of deep oil production and gas facilities. Hydrate kinetics may be divided into three main stages: nucleation, growth and agglomeration. In this work we focus on the role of hydrate agglomeration because of the important role it plays in the plug formation within condensate pipelines. To date, the accurate prediction of hydrate agglomeration has been a missing link, due to scarcity of experiments and inherent difficulties in making agglomeration measurements.

A two-dimensional DEM model (2D-DEM) is used to simulate the hydrate agglomeration in pipe flow. The 2D-DEM model generates a detailed solution of the equations of motion for an interacting multi-body system, which describes the evolution of the interaction forces, stresses, velocities and positions of the hydrate particle system over time.

To model the hydrate agglomeration the following forces are applied:

- An attractive van der Waals inter-particle interaction force

- An attractive capillary inter-particle interaction force

- A repulsive contact elastic and damping inter-particle interaction force

- A fluid-particle drag force based on the Stokes' law

The analyses predicted that no significant agglomeration occurred when only van der Waals forces are considered. However, when an additional capillary force field was modeled, significant agglomerating behavior was predicted. The size of agglomeration was simulated and verified with existing data. The simulation results depend on the volumetric fraction of particles and shear rates.

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1. Introduction

Gas hydrates are the solid solutions of gas components and water. Since Hammerschmidt (1934) discovered the formation of hydrates in natural gas systems. Hydrates in pipelines have been of major interest in the oil and gas industry. Recent industrial developments have concerned deep-water production at seafloor depths of 1-3 km and temperatures between -2 to 4°C (Gudmundsson, 2002), conditions which encourage hydrate plug formation.

There have been several studies on kinetics of hydrate formation. Those previous studies can be categorized into two main subjects: nucleation and growth. In contrast to previous studies, gas pipelines hydrate agglomeration plays an important role. After the breakup of the hydrate film along the interface, hydrate particles agglomerate to form a hydrate plug (Lingelem et al., 1993).

Recently a novel technique using turbidity meters has been applied to the hydrate kinetics and showed insight into hydrate particles. Herri et al. (Herri et al., 1999) analyzed the particle size distribution of hydrate particles with the particle balance equations and a mass transfer model. However it remains a difficult problem to describe agglomeration from experimental observation for various reasons. Firstly the particles start to agglomerate just after the nucleation process (Mersmann, 2002). Secondly, the observed particle size distribution is a result of kinetic contributions such as nucleation, growth, agglomeration, breakage, and attrition. In colloidal science there have been studies on the viscosity and the particle agglomeration (Mersmann, 2002).

Different approaches have attempted to measure the relative viscosity which can be analyzed as the product of agglomeration. Camargo and Palermo (2002) measured relative

viscosity of hydrate suspension by a co-axial viscometer. In Camargo and Palermo's work the agglomeration of the particles were calculated by the Mills' model (Mills, 1985). However, the Mill's model assumes that all the particles are in the same size and therefore cannot be applied to a non-uniform, complex particle size distribution.

An alternative way is to investigate particle agglomeration phenomena with computer simulation. The Discrete Element Method (DEM) is a computational method, which simulates the discrete mechanical behavior of a system of particles. The numerical integration of the equations of motion of the particle system in the DEM predicts the evolution of the particle system motion and interaction forces with time. Recently the DEM has been applied to cohesive clay particle systems (Anderson et al., 2000). In this work hydrate agglomeration is simulated via DEM. The size of the hydrate clusters were calculated and compared with the theoretical value from Mill's model.

To include the interaction between the fluid and the particles, this research will progress to a combination of the DEM and a Computational Fluid Dynamics (CFD). The CFD calculation, which models the viscous fluid flow, is based on the SIMPLE algorithm proposed by Patankar (Patankar, 1980) to solve the Navier-Stokes equation. The main outcome of this new approach will be the prediction of relative viscosity in hydrate suspension.

2. Theory

The Discrete Element Method (DEM) is a promising technique to simulate the mechanical behavior of a particle system immersed in a fluid. In this work a two-dimensional DEM by Mustoe (Mustoe and Miyata, 2001) was used to simulate hydrate

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agglomeration. The method is based on a numerical solution of the equations of motion for a multi-body system, integrated with respect to time. According to Newton's second law, the translational equation of motion for the center of mass is given by,

$$m\ddot{\vec{r}} = \sum \vec{F} \qquad (1)$$

where m is the mass of body, $\ddot{\vec{r}}$ is the translational acceleration vector and $\dot{\vec{r}}(=\vec{v})$ is the velocity of the hydrate particle. The equation of motion written in component form is:

$$m\ddot{x} = \sum F_x \ , \ m\ddot{y} = \sum F_y \qquad (2) \text{ and } (3)$$

Similarly the rotational equation of motion is written as,

$$I\ddot{\theta} = \sum M \qquad (4)$$

where I is moment of inertia of body and $\ddot{\theta}$ is angular acceleration and M is rotational moment.

3. Simulation for hydrate agglomeration in a co-axial viscometer

Recently Camargo and Palermo (2002) presented rheological properties of a hydrate suspension in an asphaltenic crude oil, measured with a co-axial viscometer. They also studied the rheological model by Mills (1986) which depends on the size of the hydrate clusters. In the present work Camargo and Palermo's experiments were simulated by 2D-DEM.

To simulate the motion of hydrate particles in viscous fluid, the following interaction forces were considered.

- attractive van der Waals force

- attractive capillary force

- particle-particle linear elastic contact and damping forces

- drag force based on the Stokes' law

In the DEM simulation, a specially developed shear cell was modeled. Figure 1 shows a schematic diagram of this shear cell. The small part of the Couette flow in the co-axial viscometer was represented by a shear cell with an upper moving wall and a stationary lower wall. The shear cell had periodic boundaries at the left and right sides. The velocity profile of the fluid was assumed to be proportional to the y-directional position. All the hydrate particles were assumed to be identical in size. The simulation parameters are listed in Table 1.

4. Preliminary results and discussions

The 2D-DEM program was used to simulate hydrate agglomeration in a single viscous fluid phase. Figures 2 and 3 illustrate the results. When only the van der Waals force was applied (Figure 2), no significant agglomeration was observed, while with the addition of the capillary force (Figure 3), hydrate particles agglomerated readily.

Figures 4 and 5 show the result of simulations with the same volumetric percent of particles (13.4 vol. %), but different fluid shear rates of 26.7/s and 133.3/s respectively. These figures show that the size of agglomeration is inversely dependent on shear rates.

In this work the agglomerated particle size were determined from the 2D-DEM simulation. At the steady-state the number of particles (n) for each cluster was counted.

The diameter of an agglomerated cluster was calculated from the total area of n individual particles by,

$$\frac{\pi r_a^2}{4} = n \times \frac{\pi r_p^2}{4} \tag{5}$$

where r_a and r_p is the radius of agglomerated cluster and an individual particle. The size of agglomeration from equation (5) should be smaller than the actual agglomerated size because the equation doesn't account for the volume of trapped fluid. The size of agglomeration was not measured in Camargo and Palermo's work (2002). The results of the present simulations were compared with the predicted value from Mills' model (Mills, 1985). A comparison of agglomerated sizes is shown at Table 2. Although the 2D-DEM approach cannot calculate agglomerating size exactly, the sizes obtained were the same order of magnitude and showed the same trend with shear rate as the hydrate particles in Camargo and Palermo's experimental work. In general terms, the simulated size of hydrate clusters decreases with increasing volumetric percent and with the increasing shear rate. Note this is similar to what is expected in the Mills' rheological model.

6. Improvement of the method

In our preliminary work which incorporates fluid coupling that modifies **only** the motion of hydrate particles with a fluid drag force, we were unable to predict the relative viscosity of the hydrate suspension. To overcome this restriction, we are currently developing a fully coupled fluid-particle simulation method with a combined DEM and Computational Fluid Dynamics (CFD) algorithm developed by Xu and Yu (Xu and Yu, 2002) with the addition of capillary and van der Waals force.

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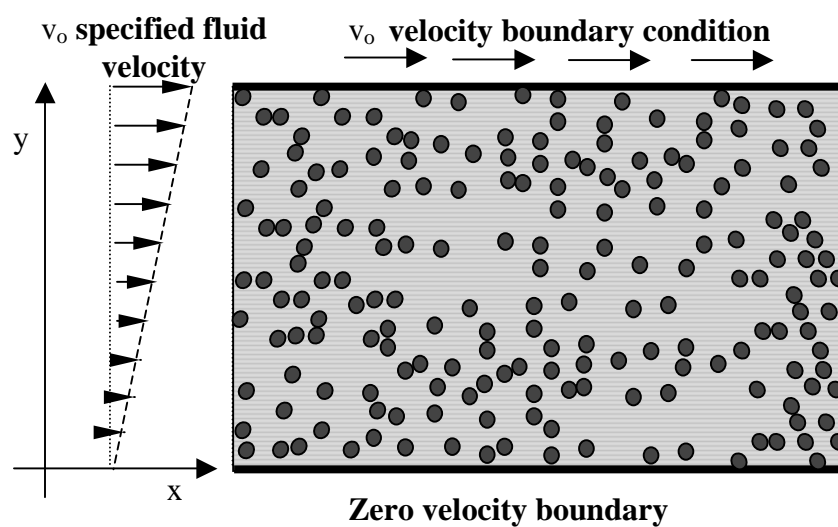
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x

Zero velocity boundary

Figure 1 Schematic diagram of the shear cell

Table 1 Specific data used in DEM simulations

Property	Value
Particle diameter	1.5 [µm]
Particle volume fraction	0.134, 0.274 [%]
Shear cell dimension	75×75 [µm×µm]
Shear rate	26.7, 133, 533 [/s]
Oil viscosity	0.03 N-s/m^2
Hamaker constant	5.1×10^{-21} [J][1]
Surface tension	10 [mN/m][2]

[1] Israelachvili (1992)
[2] Camargo and Palermo (2002)
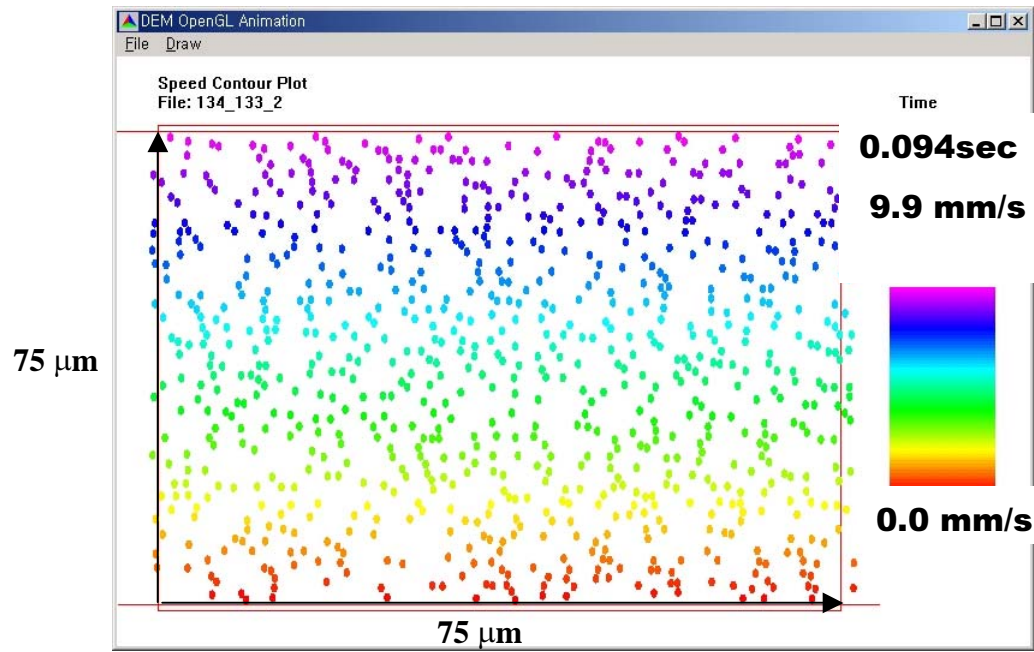
Figure 2 Simulated results of hydrate agglomeration with van der Waals force only; 13.4 vol. %, 133.3/s shear rate; Color of particle represents its speed.
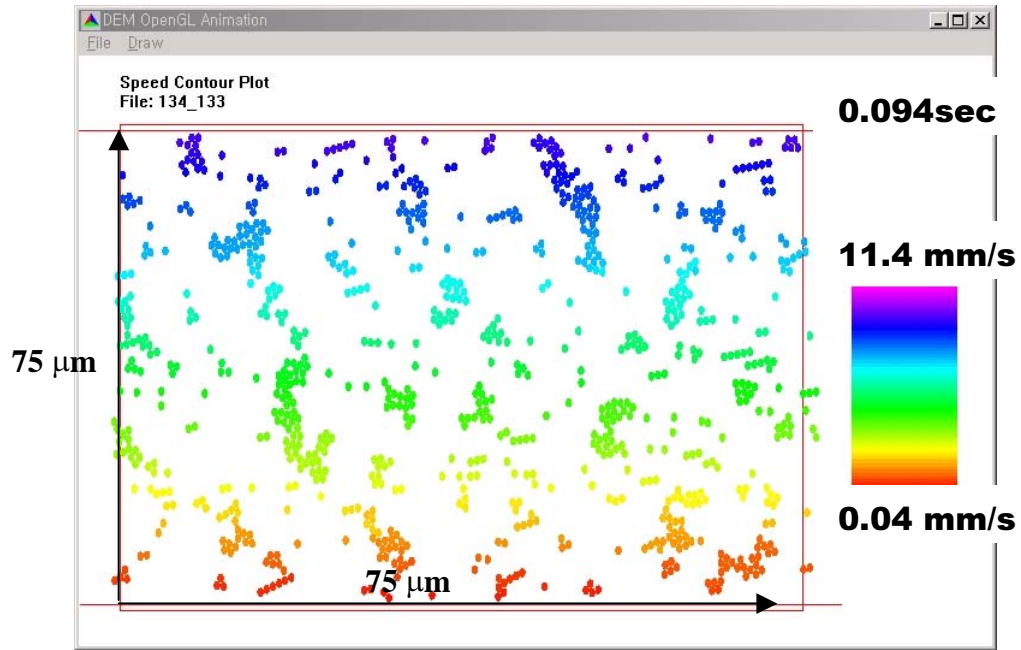
Figure 3 Simulated results of hydrate agglomeration with van der Waals force and the capillary force; 13.4 vol. %, 133.3/s shear rate; Color of particle represents its speed.
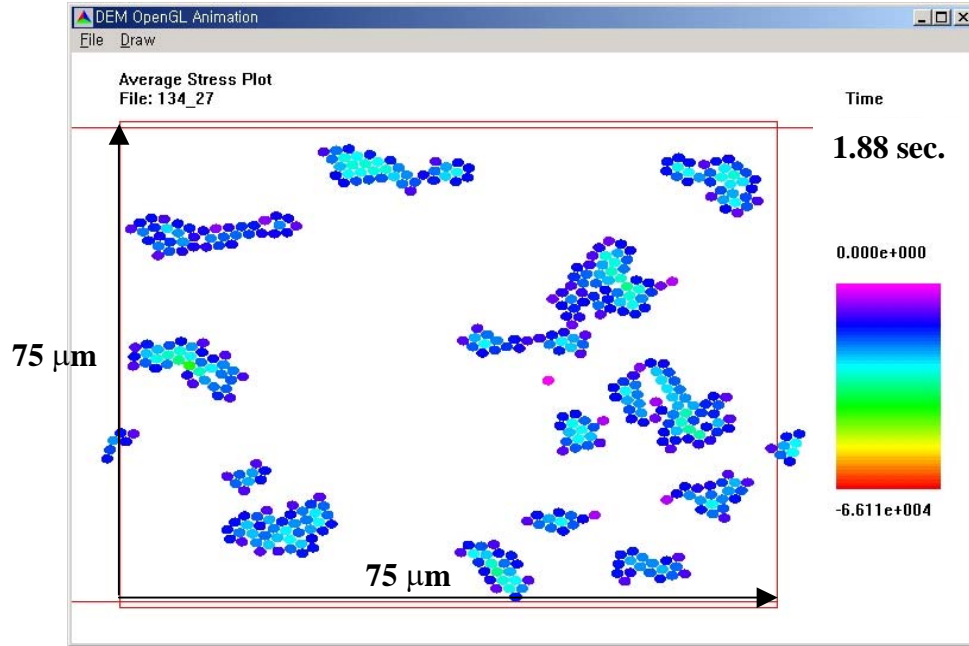
Figure 4 Agglomerated particles at steady-state, 13.4 vol. % and 26.7/s shear rate; Color of particle represents its shear stress.
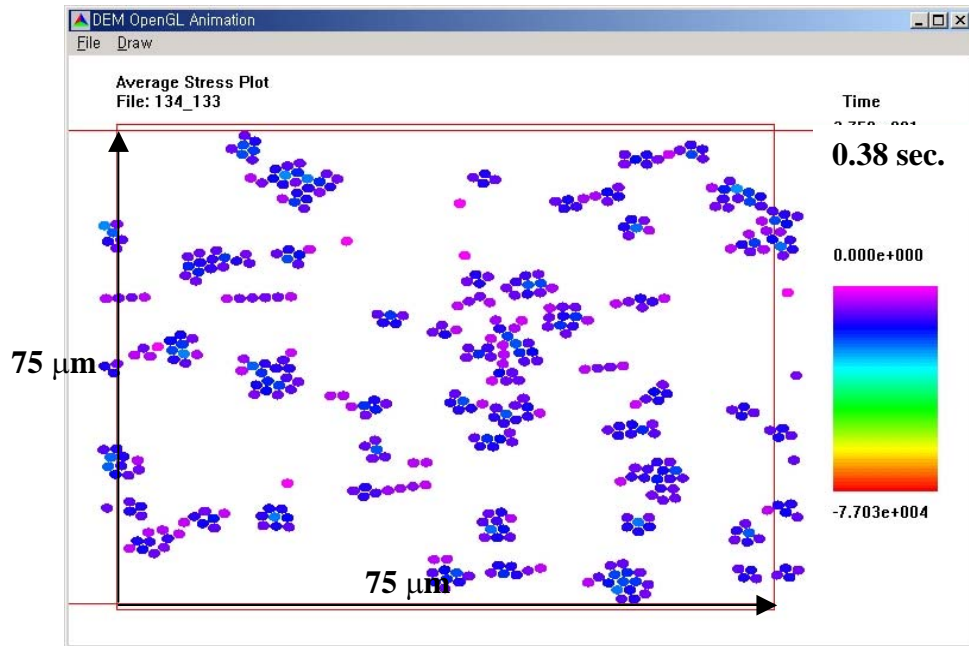
Figure 5 Agglomerated particles at steady-state, 13.4 vol. % and 133.3/s shear rate; Color of particle represents its shear stress.

Table 2 Comparison of Agglomeration Size

Hydrate Vol. %.	13.4 %		27.4 %	
Shear rate	Camargo[μm]	2D-DEM[μm]	Camargo[μm]	2D-DEM[μm]
26.7/s	13.68	7.93	4.94	7.70
133/s	9.86	3.79	4.34	2.45
533/s	5.33	1.61	3.04	1.79